

parallel to the surface 113 of the lid 90, as depicted in FIG. 1 and described herein. The exposed surface 66 of the lid 90 may further comprise portions of the fluid feed lines 97 and 99 that may pass through the lid 90 as depicted in FIG. 1 and described herein. Referring to FIG. 2, a distribution plate 40 having an exposed surface 43 may be operatively coupled to the remaining portion (not shown) of a surface of the lid 90 that may be opposite and parallel to the surface 113 of the lid 90, as depicted in FIG. 1 and described herein. The distribution plate 40 may have been operably coupled to the lid 90 by inserting fasteners through holes 6.

[0035] The distribution plate 40 further comprises "I" rings, wherein I is a positive integer greater than or equal to 2, and wherein the rings have been denoted as  $R_X$  ( $X = 1, 2, \dots, I-1, I$ ). FIG. 2 shows rings 44, 46, 48, and 41, which are respectively denoted as  $R_1, R_2, R_{I-1}$ , and  $R_I$ . The rings  $R_X$  ( $X = 1, 2, \dots, I-1, I$ ) each have a common point P (i.e. point 49 in FIG. 2) on the surface 43 of the distribution plate 40, wherein P is within each  $R_X$  for values of  $X = 1, 2, \dots, I-1, I$ . Each ring  $R_X$  is totally within each ring  $R_{X+1}$  for values of  $X = 1, 2, \dots, (I-1)$ .

[0036] Additionally, each ring  $R_X$  has a perimeter of length  $D_X$ , ( $X = 1, 2, \dots, I-1, I$ ), such that  $D_1 < D_2 < \dots, < D_I$ . Corresponding points in rings  $R_1, R_2, \dots, R_I$  are at increasing distance from the common point P. Each ring  $R_X$  ( $X = 1, 2, \dots, I$ ) has any geometrical shape such as inter alia, a circle, an ellipse, a rectangle or a square, etc.

[0037] Each ring of the I rings  $R_1, R_2, \dots, R_I$  in FIG. 2 comprises a distribution of channels 3 of a first type in which the first fluid may flow, or a distribution of channels 5 of a second type in which the second fluid may flow. There are  $n_1$  channels 3 of the first type in the I rings collectively, and there are  $n_2$  channels 5 of the second type in the I rings collectively. The first fluid from the fluid feed line 97 flows through the  $n_1$  channels 3 of the first type, and the second fluid from the fluid feed line 99 flows through the  $n_2$  channels 5 of the second type, as will be described infra in conjunction with FIG. 4. A ring that comprises channels 3 of the first type is called a ring of the first type, and a ring that comprises channels 5 of the second type is called a ring of the second type. There are  $I_1$  rings of the first type and  $I_2$  rings of the second type such that  $I_1 \geq 1, I_2 \geq 1$ , and  $I = I_1 + I_2$ . Thus the  $I_1$  rings of the first type collectively comprise the  $n_1$  channels 3 of the first type and no channels 5

exposing the surface layer to HF readily etches the surface layer, thereby exposing a remaining layer of oxide to etching by the HF. Etching to the given thickness is difficult to control because the formation of  $\text{SiF}_4$  continues until the surface layer, i.e., the oxide layer, has been completely etched due to formation and evaporation of  $\text{SiF}_4$ .

[0029] According to Jeng et al., the reaction of HF with  $\text{SiO}_2$  when in contact with condensed ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ) is similar to the reaction in aqueous solution,  $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$ . However, instead of being released to the solution, the  $\text{SiF}_4$  product is trapped and reacts within the condensed film to produce  $(\text{NH}_4)_2\text{SiF}_6$ . The  $(\text{NH}_4)_2\text{SiF}_6$  is observed in IR spectra of reacted layers. Microbalance results also show the presence of the reacted layer. Condensation of  $\text{NH}_3$  and HF followed by desorption of the unreacted excess produces a frequency decline of 101 Hz, corresponding to reaction of 84 Å of the several thousand angstrom thick layer of  $\text{NH}_5\text{F}_2$  that initially condensed. After heating to  $100^\circ\text{C}$  there is a 103 Hz increase of resonant frequency corresponding to 58 Å of  $\text{SiO}_2$  being etched from the adapted surface layer of the silicon wafer.

[0030] Thermal desorption spectra are consistent with  $\text{SiF}_4$  released upon thermal decomposition of the reacted layer of ammonium hexafluorosilicate. The ammonium hexafluorosilicate layer can also be removed by rinsing in a solvent, such as water.

[0031] According to Jeng et al., the amount of  $\text{SiO}_2$  which may be etched may be controlled by providing a stoichiometric number of moles of HF to  $\text{NH}_3$  needed to form ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ), i.e. providing a molar ratio of HF to  $\text{NH}_3$  in the gas above the  $\text{SiO}_2$  surface substantially equivalent to 2. Pure HF etches  $\text{SiO}_2$  with no self-limiting process. Ammonia ( $\text{NH}_3$ ) is necessary to form the hexafluorosilicate product.

[0032] Jeng et al. discloses an apparatus and method in which ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ) vapors can evaporate from an  $\text{NH}_5\text{F}_2$  effusion cell, leading to a non-stoichiometric  $\text{NH}_5\text{F}_2$  on the adapted surface layer being etched. An object of the present invention is to provide an apparatus and method in which the stoichiometric molar ratio of  $\text{HF}:\text{NH}_3 = 2$  needed to form  $\text{NH}_5\text{F}_2$  may be substantially uniformly and homogeneously provided on the adapted surface layer being etched.

and wherein a depth of the groove 121 from the surface 42 to the bottom wall 54 may be at least 0.078 in. The groove 121 may include an o-ring or equivalent seal 123, wherein the seal 123 may prevent commingling of the first and second fluids in the  $n_1$  channels 3 of the first type and the  $n_2$  channels 5 of the second type respectively. An objective of the present invention is to have  $\text{NH}_3$  and HF, inter alia, enter chamber 7 without pre-mixing. O-rings or equivalent seals 123 are used as barriers to prevent the fluids in each ring  $R_X$  from mixing. The o-ring or equivalent seals 123 may be made from polytetrafluoroethylene or fluorinated ethylene propylene such as Teflon®, acetal homopolymer resin modified with DuPont®, Kevlar® resin such as Delrin®, polyimide materials such as Vespel® or Altymid®, polyetherimide materials such as Ultem®, polyarylate such as Ardel®, polycarbonate such as Lexan®, and combinations thereof. The first and second fluids may be sent to alternating rings (i.e., the first and second fluids may be sent to rings  $R_1, R_3, R_5, \dots$  and  $R_2, R_4, R_6, \dots$ , respectively) so that as the first and second fluids respectively exit the channels 3 and 5 of each ring, there is no commingling of the first and second fluids until they enter the chamber 7 through the channels 3 and 5 of each ring.

[0045] The apparatus 10 further comprises a workpiece 30, wherein a portion 32 of the workpiece 30 has been adapted for being etched, and a remaining portion 31 has not been adapted. The workpiece 30 may comprise any semiconductor material such as silicon or germanium. The adapted surface layer 32 may be formed by oxidation of the silicon or germanium using any appropriate method of oxidation. For example, the adapted surface layer 32 of the workpiece 30 may be an oxide formed from tetraethoxysilane (TEOS) or alternatively from thermal oxidation. The workpiece 30 may be held in place by the electrostatic chuck 110.

[0046] A self-limiting etchable layer 50, having a surface 26, comprising ammonium hexafluorosilicate ( $(\text{NH}_4)_2\text{SiF}_6$ ), has been formed from a portion of the adapted surface layer 32 of the workpiece 30, wherein a remaining portion 37 of the adapted surface 32 has become impervious to etching by the first or second fluid, such as hydrogen fluoride (HF), because the remaining portion 37 has been protected from HF by the self-limiting layer 50, as disclosed by Jeng et al. in U.S. Patent 5,282,925, described herein.

[0047] A thickness of the self limiting layer 50 may be controlled, wherein a change of  $1\text{Å}$  in a temperature of the workpiece 30 equals a  $17\text{ Å}/\text{°C}$  etch rate change/minute, wherein the etch rate is directly proportional to the increase in temperature, in the temperature range from about  $-10$  to about  $90\text{Å}^\circ\text{C}$ . A temperature controlling device 180 such as, for example, an aluminum cathode may be provided to maintain the temperature of the workpiece 30 within  $\pm 1\text{Å}^\circ\text{C}$  in the range from about  $-10$  to about  $90\text{Å}^\circ\text{C}$ . The apparatus 10 further comprises a base flange 34 for supporting the temperature controlling device 180. The chamber wall 9 may also be provided with heating or cooling lines 104 to maintain the chamber wall 9 from about  $-10$  to about  $90\text{Å}^\circ\text{C}$ .

[0048] Prior to forming the self-limiting etchable layer 50, the distribution plate 40 has been aligned over the adapted surface layer 32 of the workpiece 30. Hereinafter, "aligning the distribution plate 40" or "centering the distribution plate 40" or "the distribution plate 40 has been aligned" over the adapted surface layer 32 of the workpiece 30 means the center 163 of the cavity or groove 33, the center point 49 on the surface 43 of the distribution plate 40, the center 1 of the apparatus 10, and the center 165 of the workpiece 30 are located as points on a line 56, wherein the line 56 may be orthogonal to the surfaces 42 and 43 of the distribution plate 40 and the adapted surface layer 32 of the workpiece 30. The center 1 of the chamber 7 may be found at an intersection of transversal lines 57. The center 49 of the surface 43 of the distribution plate 40, and the center 26 of the workpiece 30 may be determined to be at an intersection of the respective transversal lines.

[0049] In addition to aligning the distribution plate 40 prior to forming the self-limiting etchable layer 50, the distribution plate 40 may be positioned a distance T from the adapted surface layer 32 of the workpiece 30. In an embodiment of the present invention, the distance T from the surface 26 of the adapted surface layer 32 of the workpiece 30 to the surface 43 of the distribution plate 40 includes from about  $1/8$  in. to about  $3\text{ Å}1/2$  in.

[0050] The chamber 7 of the apparatus 10 further comprises: the surface or sandwich 119 of the electrostatic chuck 110; the upper annular ring 103; the cathode insulator 105; and the lower annular ring 125, containing a plurality of exhaust holes 127 for

polyimide materials such as Vespel® or Altymid®, polyetherimide materials such as Ultem®, polyarylate such as Ardel®, polycarbonate such as Lexan®, and combinations thereof.

[0051] FIG. 5 depicts a cross-sectional view taken along line 5-5 of FIG. 4 of a center portion of the distribution plate 40 in which the cavity or groove 33 and the  $n_1$  channels 3 of the first type in the distribution plate 40 are substantially in the same plane. The  $n_1$  channels 3 of the first type have been adapted to provide a line or path 162 or 167 for a first fluid to flow from the surface 43 of the distribution plate 40 at an angle  $\hat{I}_1$  with respect to the surface 43, wherein angle  $\hat{I}_1$  is at least 45 degrees and less than 90 degrees. The  $n_1$  channels 3 of the first type have been adapted to provide a line or path 162 or a line or path 167 for a first fluid to flow from the surface 43 of the distribution plate 40 at the angle  $\hat{I}_1$ . The first fluid flows through the  $n_1$  channels 3 of the first type along the line or path 162 or the line or path 167 drawn through a center 77 of the  $n_1$  channels 3 of the first type.

[0052] FIG. 6B depicts a cross-sectional view taken along line 6-6 of FIG. 4 of a portion of the distribution plate 40 in which the cavity or groove 55 and the  $n_2$  channels 5 of the second type in the distribution plate 40 are substantially in the same plane. The  $n_2$  channels 5 of the second type have been adapted to provide a line or path 175 for a second fluid to flow from the surface 43 of the distribution plate 40 at an angle  $\hat{I}_2$  with respect to the surface 43, wherein  $\hat{I}_2$  is at least 45 degrees and less than 90 degrees. The  $n_2$  channels 5 of the second type have been adapted to provide a line or path 175 for a second fluid to flow from the surface 43 of the distribution plate 40 at the angle  $\hat{I}_2$ . The second fluid flows through the  $n_2$  channels 5 of the second type along the line or path 175 drawn through the center 79 of the  $n_2$  channels 5. The angle  $\hat{I}_1$  (see FIG. 5) may be greater or less than  $\hat{I}_2$  or the angle  $\hat{I}_1$  may be substantially equal to  $\hat{I}_2$ .

[0053] FIG. 6A depicts FIG. 6B, wherein three dimensional XYZ axes are superimposed on the cross-sectional view depicted by FIG. 6B, taken along line 6-6 of FIG. 4. The cross-sectional view is a view of the distribution plate 40, wherein an X axis is parallel to the surfaces 42 and 43 of the distribution plate 40, a Y axis is perpendicular to the X axis in the same plane as the X axis and a Z axis, orthogonal to the X and Y axes

and to the cross-sectional view of the distribution plate 40. The right triangle ABO is in the XY plane. The line AB of the right triangle ABC is also in the XY plane. However, the line or path 175 drawn through the center 79 of the  $n_2$  channels 5 of the second type may be offset by an angle DAC 215 equal to  $\hat{I}_{\pm 2}$  with respect to the plane XY as it exits the surface 43 of the channels 5. The same line or path 175 drawn through the center 79 of  $n_2$  channels 5 of the second type may be offset by an angle BAC 220 equal to  $\hat{I}_{\pm 2}$  with respect to the XY plane. The offset angles  $\hat{I}_{\pm 2}$  and  $\hat{I}_{\pm 2}$  with respect to the plane XY may be from about 0 to -45 and about 0 to +45 degrees with respect to the XY plane of the cross-sectional view.

NO



[0054] Alternatively, by analogy to offsetting the line or path 175 drawn through the center 79 of the  $n_2$  channels 5 of the second type by the angle DAC 215 equal to  $\hat{I}_{\pm 2}$  with respect to the plane XY as it exits the surface 43 of the channels 5 as in FIG. 6A, supra, referring to FIG. 5, the line or path 162 drawn through the center 77 of the  $n_1$  channels 3 of the first type may be offset by an angle equal to  $\hat{I}_{\pm 1}$  by analogy to the angle DAC 215 with respect to the XY plane, as depicted in FIG. 6A. The same line or path 162 drawn through the center 77 of  $n_1$  channels 3 of the first type may be offset by an angle equal to  $\hat{I}_{\pm 1}$  by analogy to the angle BAC 220 with respect to the XY plane, as depicted in FIG. 6A. The offset angles  $\hat{I}_{\pm 1}$  and  $\hat{I}_{\pm 1}$  with respect to the plane XY may be from about 0 to -45 and about 0 to +45 degrees with respect to the XY plane of the cross-sectional view.

[0055] Referring to FIGS. 5 and 6B, offsetting the angle  $\hat{I}_{\pm 1}$  by  $\hat{I}_{\pm 1}$  and  $\hat{I}_{\pm 1}$  and the angle  $\hat{I}_{\pm 2}$  by  $\hat{I}_{\pm 2}$  and  $\hat{I}_{\pm 2}$  respectively, increase mixing of the first and second fluids after they have been introduced into the chamber 7, as depicted in FIG 4 and described herein. Referring to FIG. 4, a flow distribution pattern of fluids from channels 3 and 5 may flow from the surface 43 through the space or gap 107 and exhaust holes 127. In theory, the flow pattern forms a vortex flow distribution which further increases mixing of the two fluids. Referring to FIGS. 5 and 6B, it has been determined that a more uniform thickness of the self-limiting layer 50 resulted when the lines or paths 162, 167 and 175 have been directed at angles  $\hat{I}_{\pm 1}$  or  $\hat{I}_{\pm 2}$  that may be at least 45 degrees and less than 90 degrees with respect to the surface 43, wherein the angle  $\hat{I}_{\pm 1}$  has been offset by  $\hat{I}_{\pm 1}$  and  $\hat{I}_{\pm 1}$  or the angle  $\hat{I}_{\pm 2}$  has been offset by  $\hat{I}_{\pm 2}$  and  $\hat{I}_{\pm 2}$ , than if the lines or paths 162, 167 and 175 have been directed orthogonal to the

surface 43.

[0056] Referring to FIG. 4, the cavity or groove 33 and the  $n_1$  channels 3 of the first type and cavity or groove 55 and the  $n_2$  channels 5 of the second type may be formed in the distribution plate 40, such as by mechanical drilling, laser drilling or a chemical process.

[0057] Referring to FIGS. 5 and 6B, the flow rate (F) of the first or second fluid through the  $n_1$  channels 3 of the first type and the  $n_2$  channels 5 of the second type may be proportional to factors such as the pressure of the first and second fluids, the pressure (vacuum) in the chamber, described herein in text associated with FIG. 2. In addition it may be determined that F is inversely proportional to a volume (V) of the  $n_1$  channels 3 of the first type or the  $n_2$  channels 5 of the second type. The inversely proportional relationship between F and V of the channels 3 and 5 may be expressed by the following formula 1:

[0058] 1.  $F = 1/V$

[0059] V may be calculated if the channels 3 and 5 are cylindrical, wherein  $V = \pi R^2 H$ , wherein  $2R_3$  = a diameter ( $D_3$ ) of the  $n_1$  channels 3 of the first type or  $2R_5$  = a diameter ( $D_5$ ) of the  $n_2$  channels 5 of the second type and wherein H is equal to a height of the cylinder. The inversely proportional relationship between F and D, and H of the channels 3 and 5 may be expressed by the following formula 1:

[0060] 2.  $F = 4/(\pi D^2 H \sqrt{\phantom{x}})$

[0061] Referring to FIG. 6B, the channels 5 may be cylindrical, having a diameter  $D_5$  and a height  $H_5$  described by the length of a portion BE of the line or path 175. By analogy the channels 3 in Fig. 5 may also be cylindrical, having a diameter  $D_3$  and a height  $H_3$ . The flow rate (F) through the channels 3 or 5 will be inversely proportional to  $D^2$  and  $H_X$  (where  $X = 3$  or 5), according to Formula 2.

[0062] Referring to a right triangle AFE and a right triangle ACB in FIG. 6B,  $H_5$  of the channels 5 (or  $H_3$  of the channels 3, by analogy) is a portion BE of a hypotenuse AE of the triangle AFE when the channels 5 start at the bottom 51 of the cavity or groove 55 and  $H_5$  is the hypotenuse AE of the triangle AFE when the channels 5 extend from the